## 1. Details of Module and its structure

| Module Detail | Chemistry |
| :--- | :--- |
| Subject Name | Chemistry 01 (Class XI, Semester 01) |
| Course Name | Equilibrium: Part 1 |
| Module Name/Title | kech_10701 |
| Module Id | Definition of rate of reaction, physical and chemical processes, <br> reversible and irreversible reactions. |
| Pre-requisites | After going through this module, the learner will be able to: <br> 1. State the law of equilibrium; |
| 2. Explain characteristics of equilibria; |  |
| 3. Identify dynamic nature of equilibrium involved in |  |
| physical and chemical processes; |  |

## 2. Development Team

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## 1. Introduction

The term equilibrium is used in daily life in various contexts, such as, in a play ground where kids play at merry-go-round or see-saw they balance themselves and maintain an equilibrium so that they do not fall. While performing acrobatics or dance you keep your body in equilibrium, so that the outward and inward or upward and downward forces are balanced. The size of a balloon depends on the equilibrium achieved between the pressure outside and inside the balloon. In these cases we can experience and see the equilibrium being maintained. What about molecular systems during a physical or chemical change?
In case of change of state during evaporation in a closed container molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached equilibrium state at this stage. The rate of evaporation is equal to the rate of condensation.

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{vap})
$$

Thus, this is not a static but a dynamic equilibrium - there is a lot of activity at the boundary between the liquid and vapour phase. The double half arrows indicate that the processes in both the directions are going on simultaneously and hence the process is dynamic.

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving $\mathrm{O}_{2}$ molecules and the protein haemoglobin play a crucial role in the transport and delivery of $\mathrm{O}_{2}$ from our lungs to our muscles. The formation of oxy-haemoglobin is a reversible process. Therefore, oxygen is released and transferred to muscles.

$$
\mathrm{O}_{2}+\mathrm{Hb} \rightleftharpoons \mathrm{HbO}_{2} \text { (oxy-haemoglobin) }
$$

We will study mainly about chemical equilibrium and its characteristics in this module. The reason, as to why we should study equilibrium in chemical process lies in the study of optimum
conditions for industrial and laboratory production of chemical substances.
The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this module.

The chemical reactions may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the dynamic equilibrium and the rates of the forward and reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. It is dynamic in the sense that though there is no change in physical variables like pressure, volume, concentration , colour or temperature of the reaction mixture but at the molecular level, there is a continuous movement of molecules from reactants to products and vice-versa.

Based on the extent to which the reactions proceed, the state of chemical equilibrium in a chemical reaction may be classified into three groups :

1. The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally. For example, in the burning of wood, coal or other combustion processes the reactions are irreversible and reaction goes to completion if oxygen is sufficient.
2. The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.
3. The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc.

## 2. Equilibrium In Physical Processes

The characteristics of a system at equilibrium are better understood if we examine some physical
processes. The most familiar examples are phase transformation processes, e.g.

$$
\begin{aligned}
& \text { Solid } \rightleftharpoons \text { liquid } \\
& \text { Liquid } \rightleftharpoons \text { gas } \\
& \text { Solid } \rightleftharpoons \text { gas }
\end{aligned}
$$

## Solid-Liquid Equilibrium

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273 K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K .

It is obvious that ice and water are in equilibrium only at a particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance. The system here is in dynamic equilibrium and we can infer the following:
(i) Both the opposing processes occur simultaneously.
(ii) Both the processes occur at the same rate so that the amount of ice and water remains constant.

## Liquid-Vapour Equilibrium

This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig.1). Initially
there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box.


Fig. 1 Measuring equilibrium vapour pressure of water at a constant temperature

The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained i.e.,
rate of evaporation= rate of condensation

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{vap})
$$

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point.

If we expose three watch glasses containing separately 1 mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence
the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at $100^{\circ} \mathrm{C}$ in a closed vessel. The boiling point of water is $100^{\circ} \mathrm{C}$ at 1.013 bar pressure. For any pure liquid at atmospheric pressure (1.013 bar) the temperature at which the liquid and vapour are at equilibrium is called the boiling point of the liquid. It depends on the atmospheric pressure. Boiling point of a liquid depends on the altitude of the place; at high altitude the boiling point decreases.

## Solid - Vapour Equilibrium

Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After a certain time, the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$$
\mathrm{I}_{2} \text { (solid) } \quad \rightleftharpoons \mathrm{I}_{2} \text { (vapour) }
$$

Other examples showing this kind of equilibrium are,

$$
\begin{aligned}
& \text { Camphor (solid) } \quad \rightleftharpoons \text { Camphor (vapour) } \\
& \mathrm{NH}_{4} \mathrm{Cl} \text { (solid) } \rightleftharpoons \mathrm{NH}_{4} \mathrm{Cl} \text { (vapour) }
\end{aligned}
$$

## Equilibrium Involving Dissolution of Solid or Gases in Liquids

## Solids in liquids

We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature.

In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution:

$$
\text { Sugar (solution) } \rightleftharpoons \text { Sugar (solid), and }
$$

the rate of dissolution of sugar $=$ rate of crystallisation of sugar.

Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

## Gases in liquids

When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.,

$$
\mathrm{CO}_{2}(\text { gas }) \rightleftharpoons \mathrm{CO}_{2}(\text { in solution })
$$

This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'.

It can be generalised that:
(i) For solid $\rightleftharpoons$ liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.
(ii) For liquid $\rightleftharpoons$ vapour equilibrium, the vapour pressure is constant at a given temperature.
(iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.
(iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 1.

Table 1: Some Features of Physical Equilibria

| Process | Conclusion |
| :---: | :---: |
| ```Liquid \(\rightleftharpoons\) Vapour \(\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{g})\) Solid \(\rightleftharpoons\) Liquid \(\mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{l})\) Solute(s) \(\rightleftharpoons\) Solute(solution) Sugar(s) \(\rightleftharpoons\) Sugar(solution) \(\operatorname{Gas}(\mathrm{g}) \rightleftharpoons \mathrm{Gas}(\mathrm{aq})\) \(\mathrm{CO}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}_{2}(\mathrm{aq})\)``` | $\mathrm{P}_{\text {H2о }}$ constant at given temperature <br> Melting point is fixed at constant pressure <br> Concentration of solute in solution is constant at a given temperature <br> [gas(aq)]/[gas(g)] is constant at a given temperature <br> $\left[\mathrm{CO}_{2}(\mathrm{aq})\right] /\left[\mathrm{CO}_{2}(\mathrm{~g})\right]$ is constant at a given temperature |

## General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:
i. Equilibrium is possible only in a closed system at a given temperature.
ii. Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
iii. All measurable properties of the system remain constant. That is, there is no change in the concentrations of various species in the reaction mixture and physical variables like pressure, volume, concentration, colour and temperature of the reaction mixture remain constant.
iv. When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 1 lists such quantities.
v. The magnitude of such quantities at any stage indicates the extent to which the reaction has proceeded before reaching equilibrium.

## 3. Equilibrium In Chemical Processes - Dynamic Equilibrium

Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is dynamic in nature as it consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,

$$
A+B \rightleftharpoons C+D
$$

With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction, Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.


Fig. 2 (take Fig. 7.2 from NCERT book)

Similarly, the reaction can reach the state of equilibrium even if we start with only C and D ; that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted
dihydrogen and dinitrogen. Fig. 3, shows that after a certain time, the composition of the mixture remains the same even though some of the reactants are still present.


Fig. 3 Depiction of Equilibrium for the formation of Ammonia

This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using $\mathrm{D}_{2}$ (deuterium) in place of $\mathrm{H}_{2}$. The reaction mixtures starting either with $\mathrm{H}_{2}$ or $\mathrm{D}_{2}$ reach equilibrium with the same composition, except that $\mathrm{D}_{2}$ and $\mathrm{ND}_{3}$ are present instead of $\mathrm{H}_{2}$ and $\mathrm{NH}_{3}$. After equilibrium is attained, these two mixtures $\left(\mathrm{H}_{2}, \mathrm{~N}_{2}, \mathrm{NH}_{3}\right.$ and $\left.\mathrm{D}_{2}, \mathrm{~N}_{2}, \mathrm{ND}_{3}\right)$ are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia $\left(\mathrm{NH}_{3}, \mathrm{NH}_{2} \mathrm{D}, \mathrm{NHD}_{2}\right.$ and $\mathrm{ND}_{3}$ ) and dihydrogen and its deutrated forms $\left(\mathrm{H}_{2}, \mathrm{HD}\right.$ and $\left.\mathrm{D}_{2}\right)$ are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition

Equilibrium can be attained from both sides, whether we start reaction by taking, $\mathrm{H}_{2}(\mathrm{~g})$ and $\mathrm{N}_{2}(\mathrm{~g})$ and get $\mathrm{NH}_{3}(\mathrm{~g})$ or by taking $\mathrm{NH}_{3}(\mathrm{~g})$ and decomposing it into $\mathrm{N}_{2}(\mathrm{~g})$ and $\mathrm{H}_{2}(\mathrm{~g})$.

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \quad 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

$$
2 \mathrm{NH}_{3}(\mathrm{~g}) \rightleftharpoons \quad \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})
$$

Similarly let us consider the reaction,

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g})
$$

If we start with equal initial concentration of $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$, the reaction proceeds in the forward direction and the concentration of $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 4). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ will increase until they all become constant when equilibrium is reached (Fig.4). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.


Fig.:4 Chemical equilibrium in the reaction $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$ can be attained from either direction

## 4. Law Of Chemical Equilibrium And Equilibrium Constant

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations?

What factors can be exploited to alter the composition of an equilibrium mixture? The last
question in particular is important when choosing conditions for synthesis of industrial chemicals such as $\mathrm{H}_{2}, \mathrm{NH}_{3}, \mathrm{CaO}$ etc.

To answer these questions, let us consider a general reversible reaction:

$$
A+B \rightleftharpoons C+D
$$

where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following equilibrium equation,

$$
K_{c}=\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}
$$

where $K_{c}$ is the equilibrium constant and the expression on the right side is called the equilibrium constant expression.
The equilibrium equation is also known as the law of mass action because in the early days of chemistry, concentration was called "active mass". In order to appreciate their work better, let us consider reaction between gaseous $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ carried out in a sealed vessel at 731 K .

$$
\begin{gathered}
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g}) \\
1 \mathrm{~mol} 1 \mathrm{~mol} \quad 2 \mathrm{~mol}
\end{gathered}
$$

Six sets of experiments with varying initial conditions were performed, starting with only gaseous $\mathrm{H}_{2}$ and $\mathrm{I}_{2}$ in a sealed reaction vessel in first four experiments (1,2,3 and 4) and only HI in other two experiments (5 and 6). Experiment 1, 2, 3 and 4 were performed taking different concentrations of $\mathrm{H}_{2}$ and / or $\mathrm{I}_{2}$, and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are given in Table 2.
Table 2:

| Experiment <br> number | Initial concentration/mol L |  |  | Equilibrium concentration/mol L ${ }^{-1}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\left[\mathrm{H}_{2}(\mathrm{~g})\right]$ | $\left[\mathrm{I}_{2}(\mathrm{~g})\right]$ | $[\mathrm{HI}(\mathrm{g})]$ | $\left[\mathrm{H}_{2}(\mathrm{~g})\right]$ | $\left[\mathrm{I}_{2}(\mathrm{~g})\right]$ | $[\mathrm{HI}(\mathrm{g})]$ |
| 1 | $2.4 \times 10^{-2}$ | $1.38 \times 10^{-2}$ | 0 | $1.14 \times 10^{-2}$ | $0.12 \times 10^{-2}$ | $2.52 \times 10^{-2}$ |
| 2 | $2.4 \times 10^{-2}$ | $1.68 \times 10^{-2}$ | 0 | $0.92 \times 10^{-2}$ | $0.20 \times 10^{-2}$ | $2.96 \times 10^{-2}$ |
| 3 | $2.44 \times 10^{-2}$ | $1.98 \times 10^{-2}$ | 0 | $0.77 \times 10^{-2}$ | $0.31 \times 10^{-2}$ | $3.34 \times 10^{-2}$ |
| 4 | $2.46 \times 10^{-2}$ | $1.76 \times 10^{-2}$ | 0 | $0.92 \times 10^{-2}$ | $0.22 \times 10^{-2}$ | $3.08 \times 10^{-2}$ |
| 5 | 0 | 0 | $3.04 \times 10^{-2}$ | $0.345 \times 10^{-2}$ | $0.345 \times 10^{-2}$ | $2.35 \times 10^{-2}$ |
| 6 | 0 | 0 | $7.58 \times 10^{-2}$ | $0.86 \times 10^{-2}$ | $0.86 \times 10^{-2}$ | $5.86 \times 10^{-2}$ |

It is evident from the experiments $1,2,3$ and 4 that number of moles of dihydrogen reacted $=$ number of moles of iodine reacted $=1 / 2$ (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$$
\left[\mathrm{H}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}=\left[\mathrm{I}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}
$$

Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$$
[\mathrm{HI}(\mathrm{~g})]_{\mathrm{eq}} /\left[\mathrm{H}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}\left[\mathrm{I}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}
$$

It can be seen from Table :3 that if we put the equilibrium concentrations of the reactants and products, the above expression is far from constant.

Table 3: Expression Involving the Equilibrium Concentration of Reactants

$$
\mathbf{H}_{2}(\mathbf{g})+\mathbf{I}_{2}(\mathbf{g}) \rightleftharpoons 2 \mathbf{H I}(\mathbf{g})
$$

| Experiments Number | $\frac{[\mathrm{HI}(\mathrm{~g})]_{\mathrm{eq}}}{\left[\mathrm{H}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}\left[\mathrm{I}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}}$ | $\frac{[\mathrm{HI}(\mathrm{~g})]_{\mathrm{eq}}^{2}}{\left[\mathrm{H}_{2}(\mathrm{~g}]_{\mathrm{eq}}\left[\mathrm{I}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}\right.}$ |
| :---: | :---: | :---: |
| 1 | 1840 | 46.4 |
| 2 | 1610 | 47.6 |
| 3 | 1400 | 46.7 |
| 4 | 1520 | 46.9 |
| 5 | 1970 | 46.4 |
| 6 | 790 | 46.4 |

However, if we consider the expression,

$$
[\mathrm{HI}(\mathrm{~g})]_{\mathrm{eq}}^{2} /\left[\mathrm{H}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}\left[\mathrm{I}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}
$$

we find that this expression gives constant value (as shown in Table :3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$, following equation:1, the equilibrium constant $\mathrm{K}_{\mathrm{c}}$ is written as,

$$
\left.\mathrm{K}_{\mathrm{c}=}[\mathrm{HI}(\mathrm{~g})]_{\mathrm{eq}}^{2}\right] /\left[\mathrm{H}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}\left[\mathrm{I}_{2}(\mathrm{~g})\right]_{\mathrm{eq}}
$$

Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for $\mathrm{K}_{\mathrm{c}}$ are equilibrium values. We, therefore, write,

$$
\begin{equation*}
\mathrm{K}_{\mathrm{c}}=[\mathrm{HI}(\mathrm{~g})]^{2} /\left[\mathrm{H}_{2}(\mathrm{~g})\right]\left[\mathrm{I}_{2}(\mathrm{~g})\right] \tag{2}
\end{equation*}
$$

The subscript ' c ' indicates that $\mathrm{K}_{\mathrm{c}}$ is expressed in concentrations of mol $\mathrm{L}^{-1}$.
At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium The equilibrium constant for a general reaction,

$$
\mathrm{a} A+\mathrm{b} \text { B } \rightleftharpoons \mathrm{c} \mathrm{C}+\mathrm{d} \mathrm{D}
$$

is expressed as,

$$
\mathrm{K}_{\mathrm{c}}=[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}} /[\mathrm{A}]^{\mathrm{a}}[\mathrm{~B}]^{\mathrm{b}}
$$

where $[\mathrm{A}],[\mathrm{B}],[\mathrm{C}]$ and $[\mathrm{D}]$ are the equilibrium concentrations of the reactants and products.
Equilibrium constant for the reaction,

$$
\begin{gathered}
4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 4 \mathrm{NO}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \text { is written as } \\
\mathrm{K}_{\mathrm{c}}=\left[\mathrm{NO}^{4}\left[\mathrm{H}_{2} \mathrm{O}\right]^{6} /\left[\mathrm{NH}_{3}\right]^{4}\left[\mathrm{O}_{2}\right]^{5}\right.
\end{gathered}
$$

Molar concentration of different species is indicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored.

Let us write equilibrium constant for the reaction,

$$
\begin{equation*}
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g}) \tag{4}
\end{equation*}
$$

as, $\mathrm{K}_{\mathrm{c}}=[\mathrm{HI}]^{2} /\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]=\mathrm{x}$
The equilibrium constant for the reverse reaction,

$$
\begin{equation*}
2 \mathrm{HI}(\mathrm{~g}) \rightleftharpoons \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}), \text { at the same temperature is, } \tag{5}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{K}_{\mathrm{c}}^{\prime}=\left[\mathrm{H}_{2}\right][\mathrm{I}] /\left[\mathrm{HI}_{2}\right]^{2}=1 / \mathrm{x}=1 / \mathrm{K}_{\mathrm{c}} \tag{6}
\end{equation*}
$$

$$
\begin{equation*}
\text { Thus, } \mathrm{K}_{\mathrm{c}}^{\prime}=1 / \mathrm{K}_{\mathrm{c}} \tag{7}
\end{equation*}
$$

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (4) is written as,
$1 / 2 \mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{HI}(\mathrm{g})$
the equilibrium constant for the above reaction is given by

$$
\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}=[\mathrm{HI}] /\left[\mathrm{H}_{2}\right]^{1 / 2}\left[\mathrm{I}_{2}\right]^{1 / 2}=\left\{\left[\mathrm{HI}_{\mathrm{J}}\right]\right\}^{1 / 2}
$$

$$
2
$$

$$
\begin{equation*}
=\mathrm{X}^{1 / 2}=\mathrm{K}_{\mathrm{C}}^{1 / 2} \tag{9}
\end{equation*}
$$

On multiplying the equation (4) by n, we get
$\mathrm{nH}_{2}(\mathrm{~g})+\mathrm{nI}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{nHI}(\mathrm{g})$

Therefore, equilibrium constant for the reaction is equal to $K_{c}{ }^{n}$. It should be noted that because the equilibrium constants $K_{c}$ and $K_{c}^{\prime}$ have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant (Table 4).

Table 4: Relations between Equilibrium Constants for a General Reaction and its Multiples.

| Chemical equation | Equilibrium Constant |  |
| :---: | :---: | :---: |
| $\begin{aligned} & \mathrm{a} A+\mathrm{b} \mathrm{Bc} \rightleftharpoons \\ & \mathrm{C}+\mathrm{dD} \end{aligned}$ |  | K |
|  |  |  |
| $\begin{aligned} & \mathrm{c} C+\mathrm{d} D \rightleftharpoons \mathrm{a} \\ & \mathrm{~A}+\mathrm{b} B \\ & \hline \end{aligned}$ | кс $^{\prime}$ | $=(1 / K)$ |
|  |  |  |
| $\begin{aligned} & \text { na } A+n b \text { B } \\ & \rightleftharpoons \mathrm{ncC}+\mathrm{ndD} \end{aligned}$ | $\text { кс }^{\prime \prime}=\left(K^{n}\right)$ |  |

## Problem 1:

The following concentrations were obtained for the formation of $\mathrm{NH}_{3}$ from $\mathrm{N}_{2}$ and $\mathrm{H}_{2}$ at equilibrium at $500 \mathrm{~K} .\left[\mathrm{N}_{2}\right]=1.5 \times 10^{-2} \mathrm{M} .\left[\mathrm{H}_{2}\right]=3.0 \times 10^{-2} \mathrm{M}$ and $\left[\mathrm{NH}_{3}\right]=1.2 \times 10^{-2} \mathrm{M}$. Calculate equilibrium constant.

## Solution:

The equilibrium constant for the reaction, $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$ can be written as,

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{c}}=-\left[\mathrm{NH}_{3}\right]^{2} \\
& {\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}} \\
& =\left(1.5 \times 10^{-2}\right)\left(3.0 \times 10^{-2}\right)^{3} \\
& =0.106 \times 10^{4}=1.06 \times 10^{3}
\end{aligned}
$$

## Problem 2:

At equilibrium, the concentrations of $\mathrm{N}_{2}=3.0 \times 10^{-3} \mathrm{M}, \mathrm{O}_{2}=4.2 \times 10^{-3} \mathrm{M}$ and $\mathrm{NO}=2.8 \times 10^{3} \mathrm{M}$ in a sealed vessel at 800 K . What will be $K_{\mathrm{c}}$ for the reaction $\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{g})$

## Solution :

For the reaction equilibrium constant, $K_{c}$ can be written as,
$\mathrm{K}_{\mathrm{c}}=$ $\qquad$ $\left[\mathrm{N}_{2}\right]\left[\mathrm{O}_{2}\right]$

$$
\begin{aligned}
& \quad \frac{\left(2.8 \times 10^{-3} \mathrm{M}\right)^{2}}{}=\left(3.0 \times 10^{-3} \mathrm{M}\right)\left(4.2 \times 10^{-3} \mathrm{M}\right) \\
& =0.622
\end{aligned}
$$

## Summary

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage, rate of forward and reverse reactions are equal. Equilibrium constant, $\mathbf{K}_{\mathrm{c}}$ is expressed as the concentration of products divided by that of reactants, each term raised to the stoichiometric coefficient. Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant.

$$
\begin{aligned}
& \text { For reaction, } a \operatorname{A}+b B \rightleftharpoons c C+d \\
& D \\
& K_{c}=[C]^{c}[D]^{d} /[A]^{d}[B]^{b}
\end{aligned}
$$

The value of equilibrium constant $K_{c}$ depends upon the form of balanced chemical equation and so it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant. The dependence of value of $K_{c}$ on form of chemical equation is summarised in Table 4.

